

CORROSION-RELATED CONSEQUENCES OF BIODIESEL IN CONTACT WITH NATURAL SEAWATER

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ABSTRACT

Experiments were designed to evaluate corrosion-related consequences of storing/transporting biodiesel in contact with natural seawater under anaerobic conditions. Coastal Key West, FL (KW) and Persian Gulf (PG) natural seawaters were used in these 60-day studies. The highest corrosion rates measured by electrochemical techniques were for unprotected carbon steel exposed to natural KW seawater with biodiesel addition. However, the deepest pits were measured in biodiesel with PG seawater. Microbial sulfide production was stimulated in both seawaters by the presence of biodiesel either as a separate phase or as a fuel-in-water emulsion. The presence of seawater influenced the chemistry of the biodiesel, contributing both sulfur and chloride.

Keywords: seawater, carbon steel, biodiesel, sulfide, microbiologically influenced corrosion

INTRODUCTION

The chemical and microbiological compositions of hydrocarbon fuels have been studied for decades. Microbiologically influenced corrosion (MIC) has been evaluated for crude and distillate fuels during all phases of exploration, transportation, storage and usage.¹ Estimated damage due to MIC in production, transport, and storage of fuel oil amounts to some hundred million dollars in the United States every year.² Russian investigators³ estimated that 30 percent of the corrosion damage in equipment used for oil exploration and production was directly attributable to MIC.

Biodiesels have different chemistries and microbiological constituents than petroleum diesel and those differences may influence reactions with materials, i.e., corrosion. Petroleum diesel is made up of hundreds of different hydrocarbon chains, with residues of sulfur and crude oil remaining after refinery processes. Biodiesel is a renewable fuel produced from vegetable oils by converting the triglyceride oils

Report Documentation Page			Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.				
1. REPORT DATE 2010		2. REPORT TYPE		3. DATES COVERED 00-00-2010 to 00-00-2010
4. TITLE AND SUBTITLE Corrosion-Related Consequences of Biodiesel in Contact with Natural Seawater			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory, Codes 7332/7303, Stennis Space Center, MS, 39529			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES CORROSION 2010, March 14-18, Henry B. Gonzalez Convention Center, San Antonio, TX				
14. ABSTRACT Experiments were designed to evaluate corrosion-related consequences of storing/transporting biodiesel in contact with natural seawater under anaerobic conditions. Coastal Key West, FL (KW) and Persian Gulf (PG) natural seawaters were used in these 60-day studies. The highest corrosion rates measured by electrochemical techniques were for unprotected carbon steel exposed to natural KW seawater with biodiesel addition. However, the deepest pits were measured in biodiesel with PG seawater. Microbial sulfide production was stimulated in both seawaters by the presence of biodiesel either as a separate phase or as a fuel-in-water emulsion. The presence of seawater influenced the chemistry of the biodiesel, contributing both sulfur and chloride.				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 18
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified		

to methyl (or ethyl) esters with a process known as transesterification.⁴ The transesterification process reacts alcohol with the oil to release three "ester chains" from the glycerin backbone of each triglyceride. The reaction requires heat and a strong base catalyst (e.g., hydroxide) for complete conversion of the vegetable oil into the separated esters and glycerin. In contrast to petroleum diesel, biodiesel contains no sulfur. In the U.S. the term "biodiesel" is standardized as fatty acid methyl ester (FAME). Biodiesel content is reported as the number of carbon atoms in the FAME backbone, e.g., FAME C17. Biodiesel mixes easily with petroleum diesel as a fuel additive. In 1998, biodiesel as a 20% blend (B-20) with petroleum diesel was designated an "alternative fuel" under the Energy Policy Act. This designation allows government fleet services to purchase B-20 for operation in normal diesel vehicles and receive credit for those vehicles. Aboard U.S. Navy ships, it is likely that B-20 will be exposed to seawater in compensated fuel ballast systems. Compensated fuel ballast systems are configured as a series of fuel tanks that automatically draw in seawater to replace fuel as it is consumed. Keeping the fuel tanks full in this manner enhances the stability of a vessel by using the weight of the seawater to compensate for ballast mass lost through fuel consumption. During refueling, fuel displaces the seawater, and the displaced seawater is discharged.

Some bacteria and fungi are naturally occurring in petroleum diesel; others are introduced as contaminants from air or water. Several investigators have reported that the microflora that persists in hydrocarbons depends on the formulation.^{5,6} The microorganisms most often associated with MIC in hydrocarbon fuels in contact with fresh water or seawater are the sulfate-reducing bacteria (SRB) and fungi (e.g., *Hormoconis resinae*).⁷ There are little data on the natural microflora in biodiesels, but Lee et al.⁸ isolated *Sphingomonas* spp. from biodiesel. Microbial interaction with both petroleum diesel and biodiesel is limited to water availability. Since water is sparingly soluble in both petroleum diesel and biodiesel, microbial growth is concentrated at fuel/water interfaces, i.e., emulsified water, and separate water phases. Biodiesel is hygroscopic, absorbing water from the atmosphere. Mono- and diglycerides left over from the reactions to produce biodiesel can act as emulsifiers, facilitating formation of persistent emulsions. The presence of water increases the possibility of abiotic corrosion, growth of microorganisms and MIC.

The experiments described in this paper examined the corrosion behavior of unprotected carbon steel exposed to pure biodiesel in the presence of two natural coastal seawaters under anaerobic conditions. In a separate series of experiments, the microbial constituents in the seawaters at the conclusion of the experiment were identified using polymerase chain reaction amplification and the oxidations products of degradation were identified.

MATERIALS AND METHODS

Metal Coupons

Corrosion coupons of UNS C10200 carbon steel (CS) (0.20% C, 0.47% Mn, 0.012% P, 0.013% Si, bal. Fe) were fabricated* to dimensions of 5/8" (1.5875 cm) diameter and 1/8" (0.3175 mm) thick (5.5 cm² total area). A wire was attached to the backside of some the coupons with conductive epoxy and carbon tape to achieve electrical connection. Coupons were individually mounted in epoxy[†] to electrically isolate the wire connection and to establish an exposed area of 2 cm². Vacuum grease prevented epoxy intrusion between the coupon face and mount bottom, preserving the as-mill finish. Mounted coupons and unmounted coupons, referred to as 'electrodes' and 'coupons' respectively, were

* Metal Samples, Munford, AL

† Epothin™, Buehler Ltd., Lake Bluff, IL

sonicated in liquid detergent, rinsed successively with acetone, ethanol and distilled water and blown dry with nitrogen (N₂) gas.

Seawater

Persian Gulf (PG) seawater was collected from the U.S. Navy pier at Mina Sulman, Bahrain. Key West (KW), FL, seawater was collected at the Naval Research Laboratory Marine Corrosion facility. PG seawater was collected within the first meter of surface seawater by immersing each collection container underwater by hand. KW seawater was collected at a depth of 1.2 – 1.5 m by intake pipes powered by suction pumps. Each seawater was shipped to the Naval Research Laboratory, Stennis Space Center, MS (NRLSSC), in three 19 L plastic containers. The pH[†] and salinity[§] were recorded immediately. PG and KW seawaters have been characterized in more detail elsewhere.⁹⁻¹³

Biodiesel

A previously characterized soy-based biodiesel was obtained from U.S. Navy Fuel and Lubes, Patuxent River, MD.⁸ The major components of the biodiesel were FAME C17 and C19.

Exposure Conditions

Two chambers were constructed to expose CS electrodes to seawaters with biodiesel additions. The chambers were cylindrical (27.9 cm dia. and 35.5 cm height) and constructed from heavy gauge, chemical resistant, opaque black plastic. The chambers have been previously used for seawater-only exposures.^{9-11,13} Chambers were sealed by clamping the lid onto a rubber gasket. In this configuration, the chambers developed their own internal atmosphere but exterior gases could still enter the container through ports if required. The ports were 3/4" (1.9 cm) ball valves at the end of 3/4" dia. x 12" long (1.9 cm dia. x 30 cm) plastic pipe. Ag/AgCl electrodes and Pt/Nb mesh were used as reference and counter electrodes, respectively. For each chamber, 9 electrodes were arranged vertically so that triplicate coupons were exposed to three conditions (from top to bottom): 1) biodiesel, 2) biodiesel/seawater interface, 3) seawater (Figure 1). A dissolved oxygen (DO) probe^{**} was placed at the bottom of the chamber.

Chambers were filled with 6 L seawater and 4 L biodiesel (one with KW and one with PG seawater) and placed in an anaerobic hood with an atmosphere of 0.01% CO₂, 10 % H₂ and the balance N₂. CO₂ concentration was chosen to maintain a seawater pH of between 7.8 and 8.2.¹⁴ Ports were closed to limit condensation inside the anaerobic hood. Anaerobic hood temperature was maintained at 23°C. No attempt was made to sterilize chambers, glassware, coupons, wires, or plastic mounts prior to introduction of fuel and water.

The pH and salinity were recorded after 60 days. DO concentration was monitored continuously at 2-hr intervals by a mini-data logger^{††} attached to the DO probe. Sulfide concentration [S²⁻] was measured after the 60-day exposure using the methylene blue method¹⁵ with a commercial analysis kit.^{‡‡}

[†] Model AR50 pH Meter, Accumet[®]

[§] Model 13-946-27 Salinity Refractometer, Fisher Scientific

^{**} Model CS510-L Oxyguard DO Probe, Point Four Systems, Inc., Coquitlam, BC, Canada.

^{††} Model Volt101, Midgetech, Inc., Warner, NH

^{‡‡} K-9510, CHEMets[®] Kit

Electrochemical Methods

A computer-controlled potentiostat/multiplexer^{§§} was used for all electrochemical measurements. Polarization resistance (R_p) was determined by the linear polarization resistance technique (LPR)¹⁶ on each electrode once a day. For each LPR scan, corrosion potential (E_{corr}) was recorded vs. the reference electrode. Current density (i [A cm^{-2}]) was recorded as the potential of each coupon was scanned from -10 mV to +10 mV vs. E_{corr} at the standard scan rate of 0.1667 mV/s (0.6 V/hr).¹⁷ R_p was determined by a least-squares-fit of the slope of the potential (V)/ i curve using Ohms Law ($R_p = V/i$). Compensation for solution resistance (R_s) was not necessary because of the relatively high conductivity of seawater¹⁸ and low current densities ($\mu\text{A cm}^{-2}$). The inverse ($1/R_p$) is proportional to the instantaneous corrosion rate. The term ‘instantaneous’ is used here to distinguish it from a cumulative corrosion rate determination such as weight loss. LPR provides the corrosion rate at the instant in time of the measurement; it provides no information of corrosion that has occurred previously.

Post-Exposure Surface Examination

After the 60-day exposure period, electrodes were removed and imaged using a macro digital camera.^{***} Each electrode was fixed in cacodylate buffered 4 % glutaraldehyde in artificial seawater and rinsed in distilled water. Corrosion morphology and corrosion product chemical composition were characterized with environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS), respectively.¹⁹ Electrodes were acid cleaned to remove corrosion products,²⁰ and re-examined with ESEM. Select electrodes were scanned using a non-contact optical profiler^{†††} with a 400 μm optical laser pen to reconstruct high contrast 3-D digital images. Pit depths were measured from these reconstructed images.

Bench Top Assay for Sulfide Production

Four experimental conditions were tested for both KW and PG seawaters:

- natural seawater only
- natural seawater and biodiesel
- natural seawater with biodiesel emulsion (fuel-in-water)
- sterilized²¹ natural seawater and biodiesel

Experiments were carried out in 150 mL flasks with 100 mL seawater and 25 mL of biodiesel (if present). Fuel-in-water emulsions were prepared by shaking seawater and biodiesel for 10 seconds, allowing distinct layers to separate over a 1 hr period and removing the separate biodiesel phase by pipette. The presence of fuel-in-water emulsions was confirmed by the cloudy appearance of the seawater. A CS coupon (5.5 cm^2) was added to each flask. Each flask was sealed and placed in the anaerobic chamber previously described. Glassware and metal samples were clean but not sterile. Exposure time was 60 days. Sulfide production was indicated by the formation of black corrosion products. Corrosion product chemical composition was characterized by ESEM/EDS.

^{§§} Gamry Instruments, Warminster, PA

^{***} Nikon Model S-700

^{†††} Nanovea Model PS50, Irvine, CA.

RESULTS

Seawater Chemistry

At the onset of the experiments, the pH values of KW and PG seawaters were 8.41 and 8.37, respectively. PG seawater had a higher salinity (44 ppt) than KW seawater (39 ppt). After 60 days exposure to biodiesel, salinities remained unchanged for all conditions and pH values of anaerobic KW and PG seawaters were 7.58 and 7.10, respectively. $[S^{2-}]$ in anaerobic KW and PG seawaters was 6 and 2 ppm, respectively, at the conclusion of the experiment. $[DO]$ (ppm) vs. time for KW seawater is shown in Figure 2. Initial $[DO]$ was 4.8 ppm. $[DO]$ reached <0.1 ppm after 1 day indicating anaerobic conditions and remained constant over the entire 60-day exposure period. Data for PG seawater were identical (not shown).

Electrochemical Behavior

Figure 3 shows $1/R_p$ ($\text{ohms}^{-1}\text{cm}^{-2}$) as a function of the 60-day exposure period for CS electrodes exposed to additions of biodiesel to 1) anaerobic KW seawater and 2) anaerobic PG seawater. Triplicate data were averaged for each electrode position, i.e., biodiesel/seawater interface and seawater, (Figure 1). Electrode position did not affect corrosion rate above an order-of-magnitude for each exposure condition. Initially, corrosion rates for KW decreased from 10^{-4} and 10^{-6} $\text{ohms}^{-1}\text{cm}^{-2}$ but at 12 days a sulfide odor was detected and corrosion rate increased to 10^{-2} $\text{ohms}^{-1}\text{cm}^{-2}$ by day 23. PG produced lower corrosion rates ($<10^{-6}$ $\text{ohms}^{-1}\text{cm}^{-2}$ average). Collection of electrochemical data for coupons immersed in biodiesel was not possible due to the very high resistivity (megaohms) of the biodiesel layer.

Figure 4 shows E_{corr} ($V_{\text{Ag/AgCl}}$) as a function of time over the 60-day exposure period for the same conditions shown in Figure 3. Throughout the exposure period, E_{corr} values in KW seawater were independent of electrode position and lower than E_{corr} values in PG seawater. Initially, E_{corr} values in KW seawater for both positions was $-0.750 V_{\text{Ag/AgCl}}$, increased to $-0.700 V_{\text{Ag/AgCl}}$ after 12 days, and dropped to near $-0.800 V_{\text{Ag/AgCl}}$ after 23 days. In contrast to exposure to KW seawater, E_{corr} values in PG seawater were highly dependent on electrode position with the biodiesel/PG seawater interface position consistently being the higher of the two. After 1 day, E_{corr} values for the PG seawater and biodiesel/PG seawater interface positions were $-0.700 V_{\text{Ag/AgCl}}$ and $-0.580 V_{\text{Ag/AgCl}}$, respectively. At day 15, both positions dropped to $-0.760 V_{\text{Ag/AgCl}}$. E_{corr} values for the PG seawater position slowly increased to $-0.730 V_{\text{Ag/AgCl}}$ over the remainder of the exposure period. E_{corr} values for the biodiesel/PG seawater interface position increased steeply to $-0.550 V_{\text{Ag/AgCl}}$ by day 37, dropped to $-0.675 V_{\text{Ag/AgCl}}$ by day 41, and slowly increased to $-0.620 V_{\text{Ag/AgCl}}$ by the end of the exposure period.

Macroscopic Inspection

After 60 days, the exposure chambers were opened. The KW chamber had a very strong putrid, sulfide smell while the smell was less pronounced in the PG chamber. A viscous, oily, cloudy layer at the biodiesel/seawater interface was observed in both chambers, but was more pronounced in the KW seawater chamber. Electrodes immersed in biodiesel (Figure 5a) retained the mill finish except for a small areas (<1 mm dia.) of black corrosion products. At the biodiesel/seawater interface (Figure 5b), differences between electrode regions exposed to biodiesel (top - dull gray) and seawater (bottom - black) were clearly observed. Black corrosion products covered the entire surface of electrodes immersed in seawater (Figures 5c).

Corrosion Product Characterization

Corrosion products in KW and PG anaerobic seawaters consisted of small nodules and significant amounts of extracellular polymeric substances (EPS). EPS were also apparent at the biodiesel/seawater interface (Figure 6a&b). Corrosion product EDS data are summarized in Tables 1 and 2 for sulfur concentration [S] and chloride concentration [Cl],^{†††} respectively. For KW exposures, average [S] for electrodes exposed to seawater, biodiesel/seawater interface, and biodiesel were 5.1, 2.2, and 3.4 wt%, respectively. Electrodes exposed to biodiesel had the largest range of [S], 0.0 – 12.7 wt%. The maximum [S] (12.7 wt%) was associated with one of the small black corrosion products areas surrounded by undisturbed mill finish. For PG exposures, the highest measured [S] was for the biodiesel exposure position with a value of 3.1 wt%. In addition, Cl⁻ was detected in some areas on electrodes exposed in biodiesel with a maximum value of 0.5 wt%. The maximum [Cl⁻] (9.0 wt%) was associated with PG electrodes at the biodiesel/seawater interface.

Corrosion Morphology

Corrosion morphology and pit depth information are summarized in Figures 7 & 8 and Table 3. Exposure to biodiesel in the presence of KW seawater (Figure 7a) resulted in a largely intact surface with pits ranging in diameters of 30 to 1000 μm . Maximum pit depth was 35 μm . The deepest pits (65 μm) were measured at the biodiesel/seawater interface, as indicated by the arrow in Figure 7b. Wider and shallower (20 μm) pits were observed below the interface in the same electrode. Exposure to KW seawater (Figure 7c) resulted in a larger number of pits than exposure to biodiesel. However, maximum pit depth was 20 μm . Exposure to biodiesel in the presence of PG seawater (Figure 8a) resulted in isolated pits (100 μm dia.) and coalesced pits with maximum depths of 75 μm surrounded by an intact, passive surface. Small diameter (10 μm) pits with maximum depths of 10 μm were not directly associated with the biodiesel/seawater interface but over the entire electrode surface (Figure 8b). Exposure to seawater (Figure 8c) resulted in the highest density of pitting, but with shallower maximum pit depth (30 μm) than exposure to biodiesel.

Bench Top Assay for Sulfide Production

Sulfide production was observed in all KW seawater exposures with natural microflora. No sulfide production (indicated by black corrosion product) was observed after 60 days in sterilized KW and PG seawaters with biodiesel (Figures 9 & 10) under anaerobic conditions. Sulfide production was observed in both seawaters with biodiesel. Exposure to anaerobic natural seawater and biodiesel resulted in black corrosion products with [S] of 34.59 and 23.13 wt% for KW and PG seawaters, respectively.

DISCUSSION

An aerobic experiment using Key West seawater and biodiesel was followed using the techniques described in this paper. The results are not included because the dissolved oxygen in the aerobic experiment decreased rapidly over time as a result of limited oxygen diffusion through the biodiesel into the water and because of oxygen-consuming aerobic respiration and corrosion reactions.

Lee et al.⁹ documented corrosion of carbon steel exposed to stagnant natural KW aerobic and anaerobic seawater and the resulting mechanisms for corrosion. Predictably, corrosion occurred under both exposure conditions. Coupons exposed to natural aerobic seawater were covered with intact iron

^{†††} While EDS does not provide valence state information, the Cl detected is assumed to be chloride (Cl⁻) from seawater, not molecular chlorine (Cl₂).

oxides and corrosion was uniform. Microorganisms were located on the surfaces, but did not appear to influence corrosion. In contrast, under anaerobic conditions, surfaces were covered with non-tenacious, microbiologically produced sulfides and localized corrosion in the form of pitting. Lee et al.⁹ also documented differences in microbial sulfide production in KW and PG seawater, but did not determine the cause of those differences. Those differences were again demonstrated in the bench top assay reported in this paper (Figures 9 and 10). Sulfide production was documented in all biodiesel separate phase seawater combinations and in fuel-in-water emulsions. Sulfide production was also observed in unamended KW seawater, but not in PG seawater.

Lee et al.⁸ demonstrated that biodiesel in contact with aerobic distilled water (simulating water of condensation) supported the growth of both bacteria and fungi in the water phase. Biodiesel does not contain sulfur and no sulfur-related microorganisms, e.g., SRB, were detected by molecular techniques in their experiments with biodiesel and distilled water. Furthermore, in their experiments with biodiesel there were no indications of corrosion, biotic or abiotic, in either the fuel or water phases. The metals used in that work were unprotected carbon steel, aluminum and a stainless steel. Lee et al.⁸ concluded that under their experimental conditions, biodiesel had the highest propensity for biofouling and the lowest corrosivity.

Corrosion in the presence of the biodiesel/seawater combination cannot be predicted from these previous experiments with the individual components, i.e., seawater and biodiesel. Biodiesel is hygroscopic, absorbing water from the environment. Microbial growth in seawater can be limited by nutrients, including carbon. Biodiesel methyl esters are quite sparingly soluble in seawater, with a saturation concentration of 7 ppm at 17 °C, but are readily biodegraded. The half-life for the biodegradation of the vegetable methyl esters in agitated San Francisco Bay water was less than 4 days at 17 °C.^{4,22}

The highest corrosion rates and lowest E_{corr} values of carbon steel in this paper were documented in exposures to anaerobic KW seawater with biodiesel. The elevated corrosion rates can be attributed to increased $[S^{2-}]$ in this exposure. Figure 11 compares instantaneous corrosion rates ($1/R_p$ [ohms⁻¹cm⁻²]) for exposures in anaerobic KW seawater with biodiesel addition (Figure 3) with results from previous work in aerobic and anaerobic KW seawater⁹ and biodiesel/aerobic distilled water.⁸ Exposure in anaerobic KW seawater with biodiesel addition resulted in the highest corrosion rates (10⁻³ ohms⁻¹cm⁻²), with the lowest rates in biodiesel/distilled water (10⁻⁷ ohms⁻¹cm⁻²). E_{corr} values (not shown) were nearly 1 V higher after 60 days exposure to biodiesel/aerobic distilled water (+0.275 V_{Ag/AgCl})⁸ when compared to E_{corr} values from exposure in aerobic KW seawater (-0.760 V_{Ag/AgCl}).⁹ Elevated E_{corr} and very low corrosion rates for carbon steel in biodiesel/distilled water indicates passive electrochemical behavior. Previous results suggested that biodiesel prevented distilled water from contacting the metal surface. In contrast, microscopic inspection of electrodes immersed in biodiesel in contact with KW and PG seawaters indicated pitting. Cl⁻ and S were detected by EDS on electrodes exposed to biodiesel, suggesting Cl⁻ and S from the seawater diffused through the biodiesel and came into contact with the electrodes. These results indicate seawater in the fuel condensed at localized areas on the electrode surfaces and in combination with Cl⁻ and/or sulfide, caused pitting. In general, black corrosion products were associated with elevated [S]. Based on prior work⁹, these black corrosion products were likely iron sulfides. EDS data are semi-quantitative and will not provide exact quantities of elements and cannot be used to determine valence state. However, EDS data were collected so that comparisons can be made between samples. Sulfide production in PG seawater required the addition of biodiesel – either as a separate phase or as a fuel-in-water-emulsion.

CONCLUSIONS

Experiments described in this paper demonstrated corrosion of unprotected carbon steel exposed in either phase of a two-phase biodiesel and seawater combination under anaerobic conditions. Corrosion in either liquid phase was influenced by the presence of the other phase. Sulfur and chloride from the seawater were located on surfaces exposed in the fuel phase and biodiesel stimulated sulfide production in the seawater phase.

ACKNOWLEDGEMENTS

This work was supported by Dr. David Shifler at the Office of Naval Research (ONR Code 332) under award N0001408WX20857. The authors would also like to acknowledge S. Williams and R. Kamin (Naval Fuels and Lubes CFT). NRL/PP/73330/09/9378.

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TABLES

Table 1. Average and maximum sulfur concentration (wt%) on CS electrode surface after 60 days exposure to seawater with biodiesel addition.

<i>Electrode Position</i>	Key West	Persian Gulf
<i>Biodiesel</i>	5.1 (12.7)	1.8 (3.1)
<i>Interface</i>	2.2 (4.0)	0.8 (2.4)
<i>Seawater</i>	3.4 (6.4)	1.3 (2.4)

Average (Maximum)

Table 2. Average and maximum chloride concentration (wt%) on CS electrode surface after 60 days exposure to seawater with biodiesel addition.

<i>Electrode Position</i>	Key West	Persian Gulf
<i>Biodiesel</i>	0 (0)	0.1 (0.5)
<i>Interface</i>	1.1 (4.1)	5.0 (9.0)
<i>Seawater</i>	0.5 (1.35)	0.7 (2.0)

Average (Maximum)

Table 3. Maximum pits depths (μm) in CS electrodes after 60 days exposure to seawater with biodiesel addition.

<i>Electrode Position</i>	Key West	Persian Gulf
<i>Biodiesel</i>	35	75
<i>Interface</i>	65 (20) ^a	10
<i>Seawater</i>	20	30

a. Shallower pits were measured in electrode below biodiesel/seawater interface

FIGURES

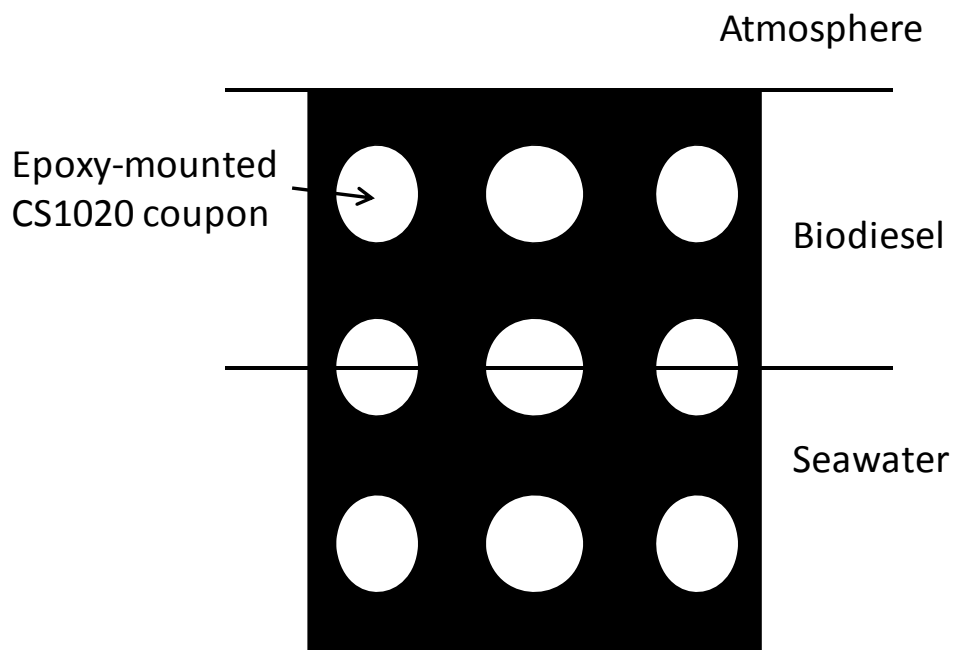


Figure 1. Schematic showing the positions of the CS1020 electrodes in relationship to the atmosphere, biodiesel, and seawater phases.

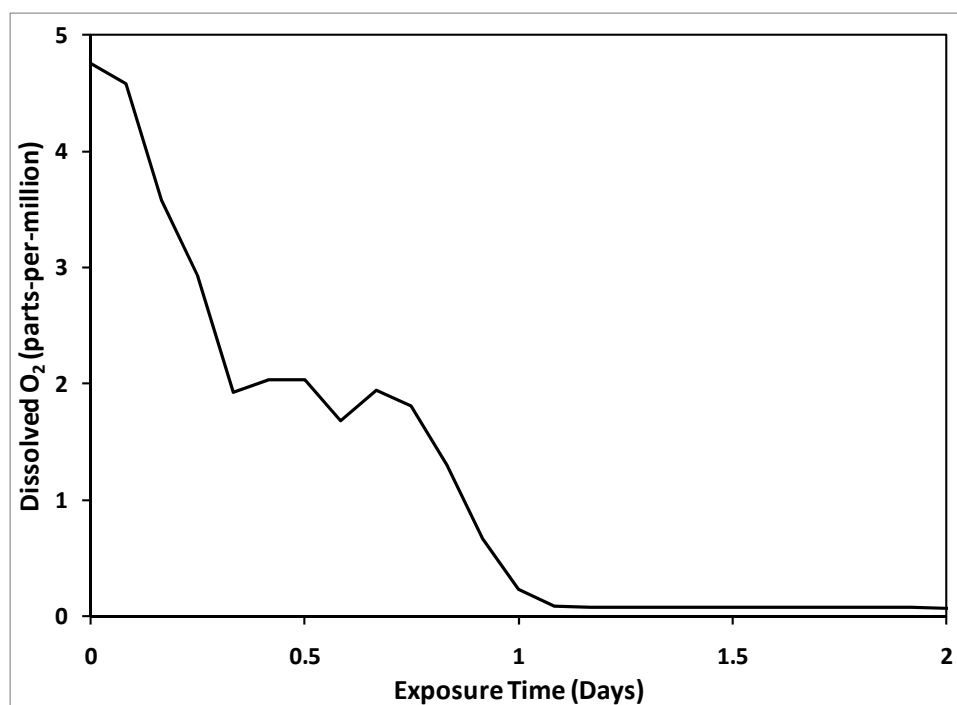


Figure 2. Dissolved O₂ concentration (ppm) of the KW seawater layer over the first 2 days of exposure.

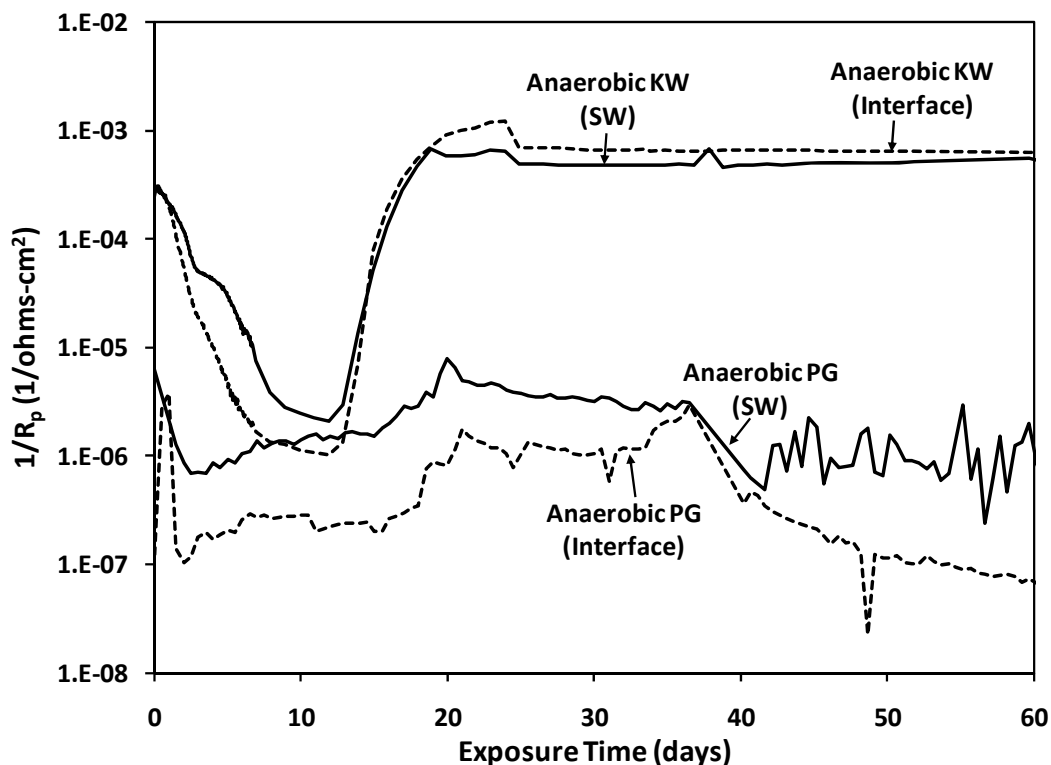


Figure 3. Logarithmic inverse R_p instantaneous corrosion rates ($\text{ohms}^{-1}\cdot\text{cm}^{-2}$) of CS1020 electrodes as a function of exposure time (days). SW = electrode immersed completely in seawater; Interface = electrode at biodiesel/seawater interface; KW = Key West; PG = Persian Gulf.

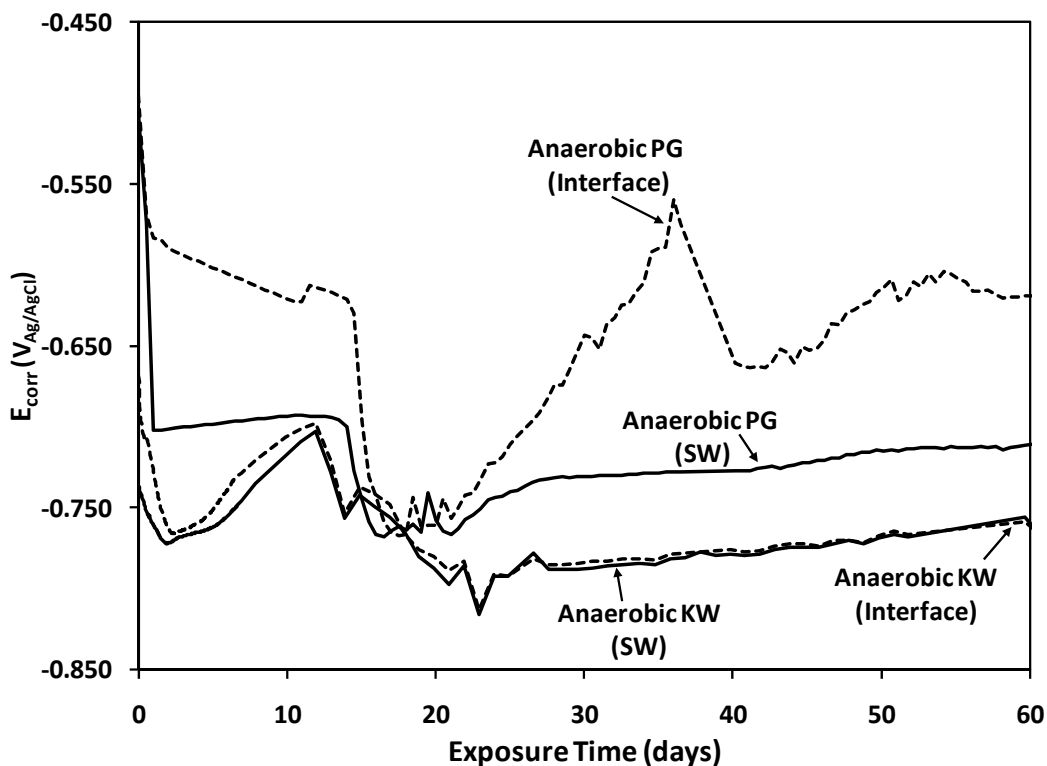


Figure 4. Corrosion potential (E_{corr} vs. $V_{\text{Ag/AgCl}}$) of CS1020 electrodes as a function of exposure time (days). SW = electrode immersed completely in seawater. Interface = electrode at biodiesel/seawater interface. KW = Key West; PG = Persian Gulf.

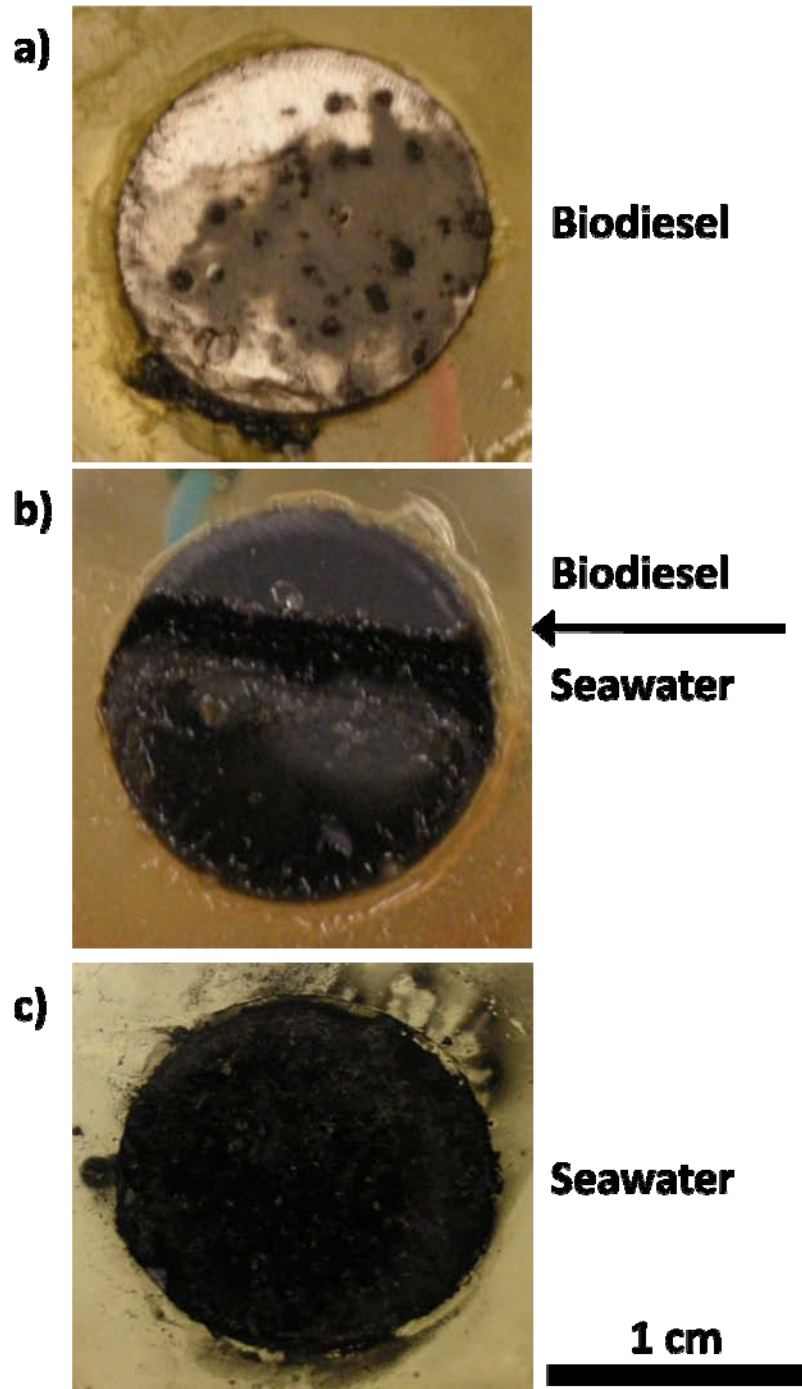


Figure 5. CS1020 electrodes after 60 days exposure in anaerobic PG seawater with biodiesel addition a) immersed in biodiesel, b) at the biodiesel/seawater interface and c) immersed in seawater.

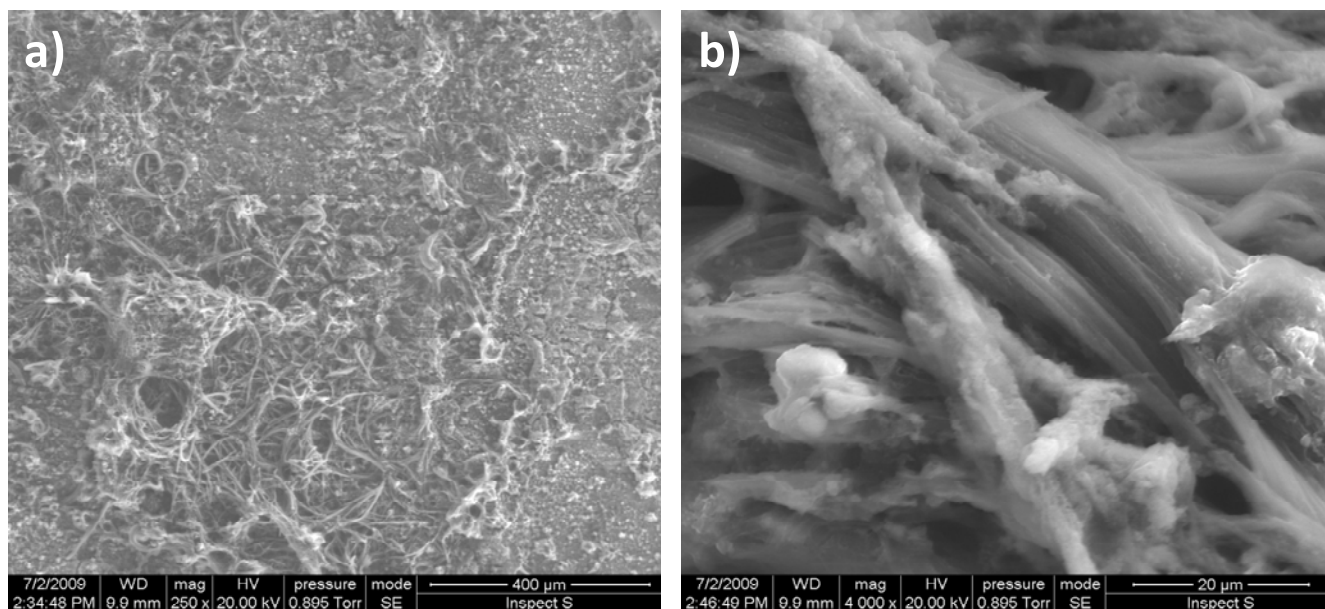


Figure 6. Micrographs of CS1020 electrode after 60 days exposure at biodiesel/anaerobic PG seawater interface shown at magnifications of a) 250X and b) 4000X.

Key West

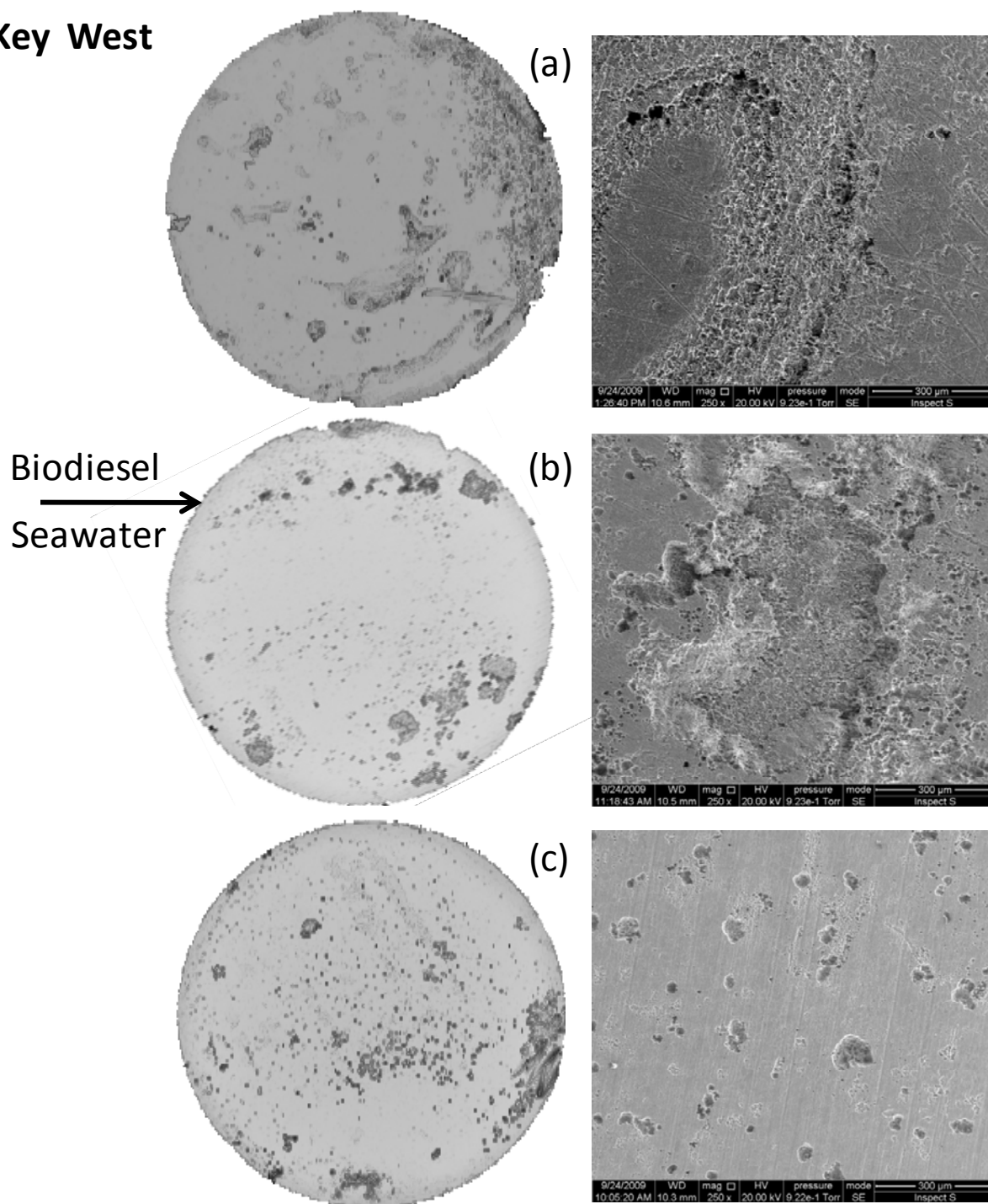


Figure 7. Acid cleaned CS1020 electrodes after exposure in anaerobic Key West seawater with biodiesel addition at electrodes positions a) biodiesel, b) biodiesel/seawater interface, and c) seawater. (Left column) Digitally reconstructed images of electrodes (1.58 cm dia.) from optical profile scans. (Right column) Micrographs of electrode surfaces (250X magnification). Arrow indicates position of biodiesel/seawater interface on the electrode.

Persian Gulf

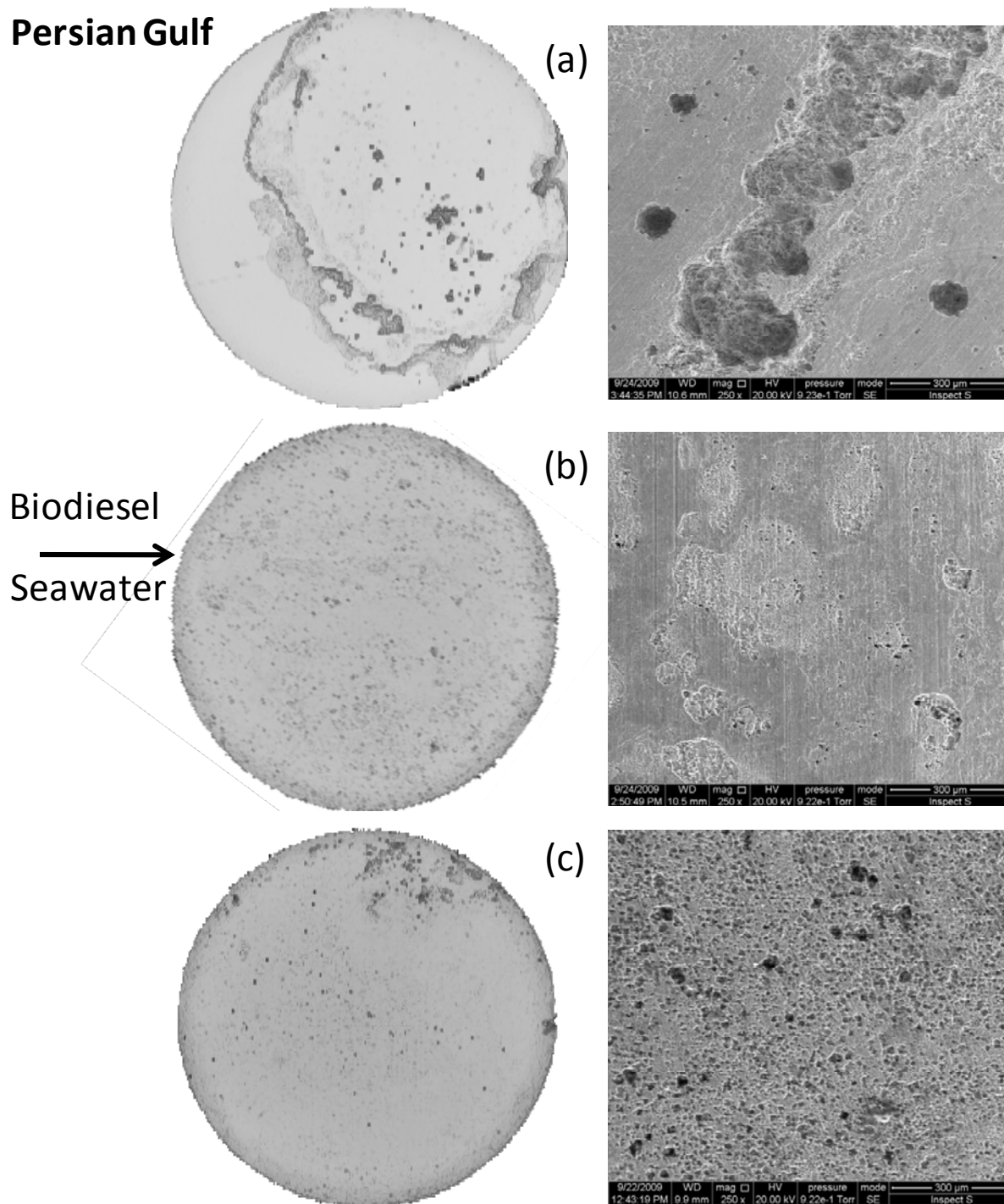
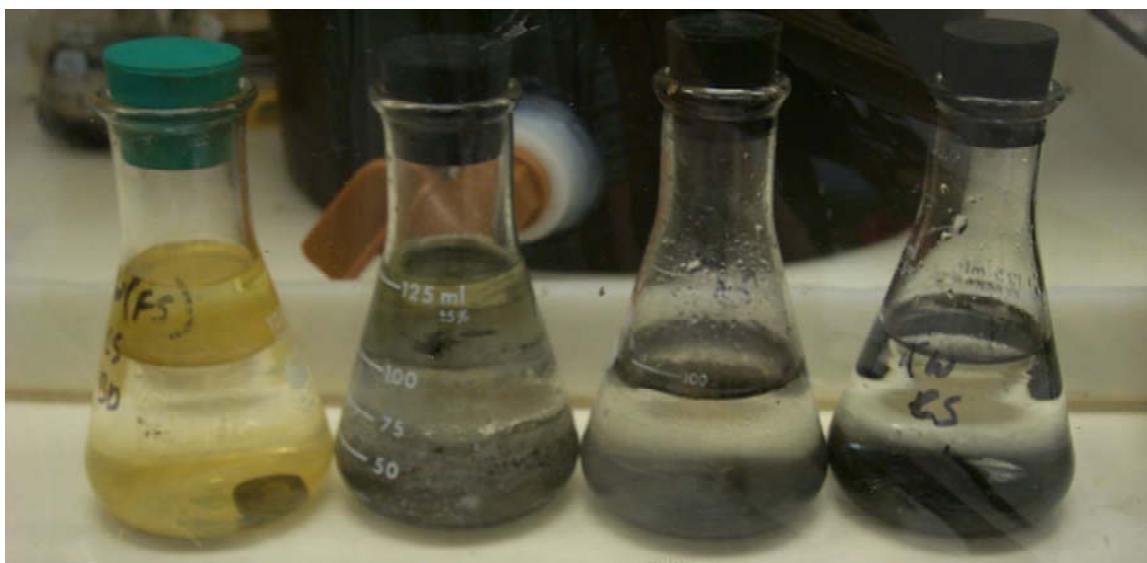


Figure 8. Acid cleaned CS1020 electrodes after exposure in anaerobic Persian Gulf seawater with biodiesel addition at electrodes positions a) biodiesel, b) biodiesel/seawater interface, and c) seawater. (Left column) Digitally reconstructed images of electrodes (1.58 cm dia.) from optical profile scans. (Right column) Micrographs of electrode surfaces (250X magnification). Arrow indicates position of biodiesel/seawater interface on the electrode.

Key West Seawater



Sterilized SW + BD

Natural SW + BD

Natural SW +
BD Emulsion

Natural SW

Figure 9. Key West seawater samples (100 ml) after 60 days anaerobic exposure with CS1020 coupon. Black color indicates the presence of sulfides. (Left to right) Sterilized seawater with biodiesel, natural seawater with biodiesel, natural seawater and biodiesel emulsion, and natural seawater without biodiesel.

Persian Gulf Seawater



Sterilized SW + BD

Natural SW + BD

Natural SW +
BD Emulsion

Natural SW

Figure 10. Persian Gulf seawater samples (100 ml) after 60 days anaerobic exposure with CS1020 coupon. Black color indicates the presence of sulfides. (Left to right) Sterilized seawater with biodiesel, natural seawater with biodiesel, natural seawater and biodiesel emulsion, and natural seawater without biodiesel.

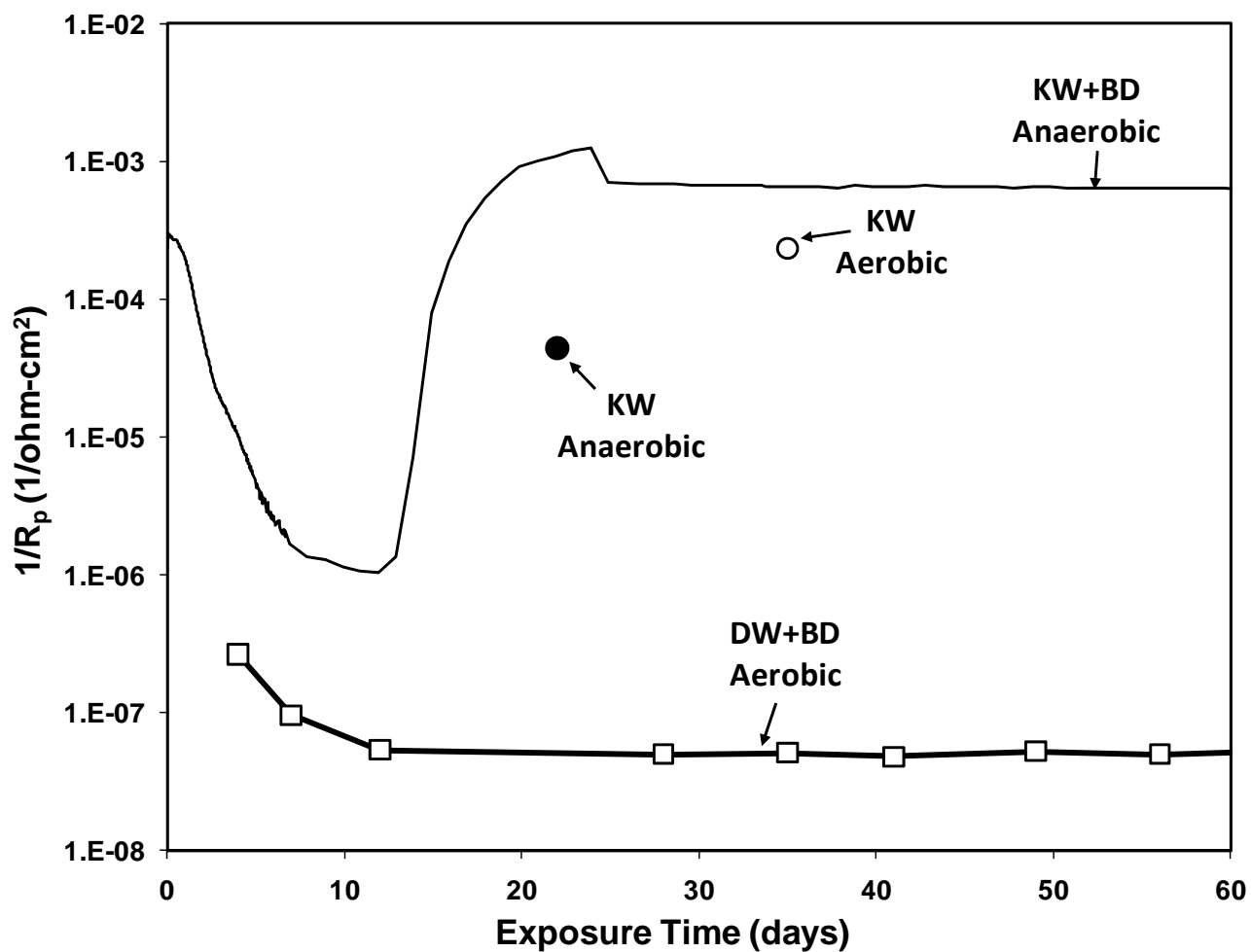


Figure 11. Composite graph of inverse R_p instantaneous corrosion rates ($\text{ohms}^{-1}\text{-cm}^{-2}$) of CS1020 electrodes on a log scale as a function of exposure time. KW+BD Anaerobic = immersion in anaerobic KW seawater with biodiesel addition from Figure 3. KW Anaerobic/Aerobic = immersion in aerobic/anaerobic KW seawater from Lee et al.⁹ DW+BD Aerobic = aerobic exposure to biodiesel/distilled water interface from Lee et al.⁸